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THE MECHANISM OF POLYVINYLAMINE WET-STRENGTHENING

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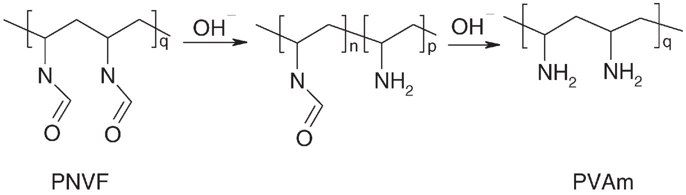
ABSTRACT

Regenerated cellulose films were laminated with polyvinylamine, PVAm, and the wet peel delamination forces were used to explore the mechanism by which PVAm increases the wet strength of paper. Conventional wet strength resins contain highly reactive chemical groups which can crosslink the resin and graft it to fibre surfaces. By contrast, it is not obvious how PVAm provides wet strength.

The delamination experiments revealed that PVAm gives strong adhesion which was approximately independent of drying temperature (23 to 110°C), pH 3 to 9, PVAm molecular weight (34,000 to 1,500,000Da), and PVAm coverage (monolayer to 70mg/m^2). By contrast the adhesion increased with the amine content of PVAm and with the degree of oxidation of the cellulose films. It is proposed that the PVAm adhesion is a combination of electrostatic and covalent bonding. The electrostatic bonding is between protonated amines, which are positively charged, and carboxyl groups on the cellulose. Whereas the covalent bonds, aminal and imine linkages, are formed between amines and aldehyde groups on the oxidized films.

INTRODUCTION

Approximately 50 years ago it was reported that polyvinylamine (PVAm), a simple polymer containing primary amine groups (see Scheme 1), increased paper wet-strength [1]. In his excellent review of wet-strength resin technology, Espy stated that the reason why a related polymer, polyethyleneimine, increased paper wet strength was unknown – the same situation is true for PVAm [2]. This paper is our first report of a fundamental investigation aimed at understanding the mechanism by which PVAm increases paper wet strength.



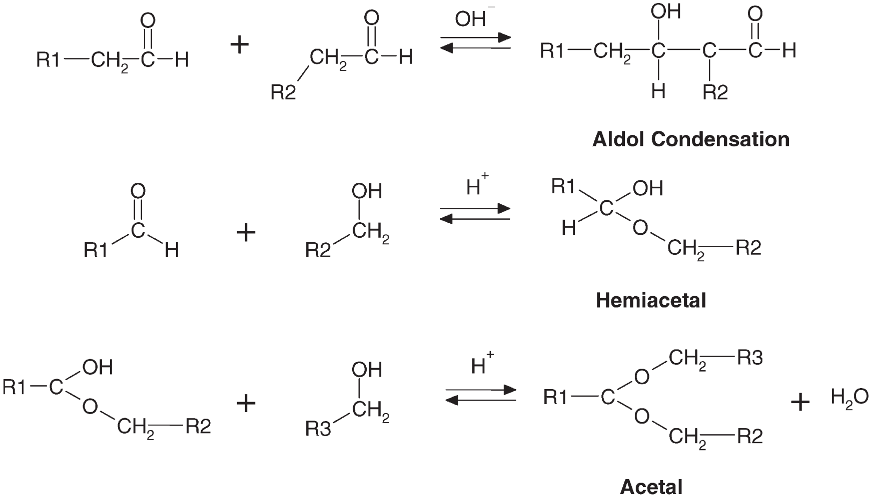
Scheme 1 The preparation of PVAm from the base hydrolysis of poly(N-vinylformamide) (PNVF).

The mechanical properties of wet paper and paperboard are important in many situations. The repulping of paper broke and paper recycling are examples of applications where the tendency of paper to disintegrate in water is an advantage. Conversely, packaging, towels and tissue require paper to maintain some level of mechanical strength when wet. There is little debate as to why wet paper is weak; the fibre-fibre joint swells in water causing it to weaken. Molecular-scale theories describing fibre-fibre bonding, including hydrogen bonding [3], van der Waals forces or interdiffusion of surface polymers [4, 5], all predict that water will weaken fibre-fibre interactions.

From a more pragmatic perspective, wet strength can be increased by either surface treatment (modification) of fibres with small molecules or by surface treatment with macromolecules, called wet strength resins. Some important conclusions from the literature are now summarized to provide a context for our new results. Waterborne molecules smaller than 1,000Da can access most of the interior surfaces in a fibre wall, whereas, high molecular weight polymers are excluded from small pores. Thus, these two classes of surface treatment chemicals are considered separately.

Fibre modification with small molecules

The presence of surface functional groups which will generate hydrolytically stable covalent bonds in the fibre joint will increase wet strength. Furthermore, if such bonds can form in the wet end of the papermachine, they will contribute to wet-web strength. Thus, aldehydes, acetals, and carboxyls will increase wet strength. Aldehydes can couple with alcohols to form acetals or hemiacetals, with other aldehydes [6] (Scheme 2), or with amines to give imines or aminals (Scheme 4). The amine reactions can occur under ambient conditions in water, potentially contributing to wet web strength [7]. In comparison, the reaction of carboxyls with alcohols to give esters, or amines to give amides, require high (120°C–180°C) temperatures with water removal.



Scheme 2 Relevant reactions of aldehydes.

Three types of fibre modification with small molecules have been described in the literature: 1) oxidation to generate surface carboxyl and aldehyde groups [8, 9, 10]; 2) surface grafting with carboxymethyl groups [11, 12], zwitterions [13], sulfonates [14] silanes [15], acetyls [16]; and, 3) polyfunctional (usually polycarboxylate) species which crosslink and thus stiffen the fibre wall [17, 18].

Finally, increasing the carboxyl contents on fibres may not only improve the wet strength directly but also increases the retention of cationic polymers and gives more grafting sites for wet strength resins. For example, poly(aminoamide)-epichlorohydrin (PAE) retention was found to correlate with the carboxyl content of the fibres [11, 19]. These authors found that the effect of oxidation and PAE content on wet strength was synergistic; although with increasing carboxyl content the pulp became more hydrophilic and thus reduced wet strength gains.

Fibre modification with macromolecules

A wide variety of polymers have been shown to have efficacy as wet strength resins [2, 20, 21] and they share some general features in contrast to the small molecules used for fibre treatment. Size scale is an obvious difference between grafting individual functional groups versus macromolecules on fibre surfaces. A monolayer of water soluble polymer on a surface will span 5 to 50nm in water whereas most functional groups, formed by oxidation or grafting of small molecules, are sub nanometre in size. Polymers can have many functional groups which, depending upon the polymer chemistry, can crosslink multiple polymer chains together to form a network. Therefore macromolecules are more likely to participate in inter-fibre bonding, which is crucial for paper strength in the wet state.

Wet strength resins are usually cationic polymers which are added in the wet end where they spontaneously adsorb on fibre and fines surfaces. If added alone, polymers will give a maximum fibre coverage corresponding to an adsorbed monolayer, which is approximately 1 mg per square meter of accessible surface [22]. When two resin-coated fibres come together in the sheet consolidation drying process, a number of interactions are possible in the fibre-fibre joint. The resin-fibre interactions may be physical (hydrogen bonding, van der Waals attraction) or chemical (covalent bonds formed through grafting). Similarly, the resin-resin interactions, dictating the cohesive strength of a resin film, can include physical and chemical bonds (covalent crosslinks).

The response to water of a wet strength resin containing fibre joint will depend upon the chemical properties of the polymer. In the extreme case, a hydrophobic polymer film such as polystyrene will not swell because it is insoluble in water. By contrast, a film based on a hydrophilic polymer, such as polyacrylamide, will dissolve in water unless it is crosslinked in which case it will swell. Examples of these two situations can be found in wet-strength resin technology. Early wet strength resins were based on hydrophobic condensation polymers of urea-formaldehyde resins and melamine-formaldehyde colloids [23]. These condensation resins crosslink upon curing to give polymer networks that are more or less insoluble. Interestingly, it seems that these chemistries do not form grafts to the fibre surfaces [24, 25, 26]. By contrast, glyoxylated polyacrylamide is an example of a resin which is hydrophilic and water soluble yet is insoluble when crosslinked and when grafted to fibres [23]. The most common wet strength resins today are PAE resins. PAE forms crosslinks by mechanisms summarized in Espy's review [2]. Espy also makes the case that PAE will graft to carboxyl groups and not to hydroxyls; this debate is not resolved and is beyond the scope of this paper [11, 27].

To summarize, wet strength requires polymer-polymer and polymer-fibre bonds to persist in the presence of water. Covalent bonds, for example, acetal and imine bonds, will hydrolyze giving temporary wet strength. The integrity of physical bonds in the presence of water is more complicated. Hydrogen bonds between alcohols are weaker than those between an alcohol and water. Thus, water disrupts untreated fibre joints based on hydrogen bonding between carbohydrates. Electrostatic attraction of a charged polymer with an oppositely charged surface is another form of physical bond. We know that these do persist in the presence of water, otherwise cationic polymer would not adsorb onto pulp. On the other hand, as pointed out by Espy [28], poly-(dimethyldiallyl ammonium chloride), (PDADMAC), a common papermaking chemical has quaternary ammonium groups which adhere to wet pulp but impart no wet strength improvement. Based on this observation, Espy argues that electrostatic bonds alone are insufficient to give wet strength improvement. It should also be noted that PDADMAC will not crosslink, so the cohesive strength of a PDADMAC film will be very low, giving low wet strength, in spite of strong adhesion to fibre surfaces.

The mechanisms by which PVAm or polyethyleneimine (PEI) increases wet strength are not obvious since neither crosslinking nor grafting seem likely. There have been some studies on PEI and PVAm wet strength and these are now reviewed.

Early studies by Trout have shown that PEI will adsorb onto pulp fibres driven by ion-exchange and that the wet strength was proportional to the amount adsorbed [29]. Sarkanen analyzed the effect of PEI on various paper properties and showed that the wet strength development was proportional to the PEI retention [30]. Interestingly, he found that when anionic polyelectrolytes were used as a retention aid the wet strength proportionality to the PEI retention was less than adding PEI alone.

Polyvinylamine (PVAm) is one of the newest polymers available to papermakers. It is manufactured in a two step procedure (see Scheme 1). The first step is the preparation of poly(N-vinylformamide), (PNVF), which is a nonionic water soluble polymer isomeric to polyacrylamide. In the second step, the amide groups are hydrolyzed to give amine groups. If the hydrolysis is complete, the product is PVAm, whereas partial hydrolysis yields a copolymer, PNVF-co-PVAm. For simplicity, we use the term PVAm to refer to both the homopolymer and the copolymer. The main features of PVAm are the molecular weight and the degree of hydrolysis which correlates with charge density.

Weisgerber's patent appears to have been the first report that PVAm gave wet strength [1]. More recently Pfohl reported a wet/dry strength ratio of 26% for a 1wt% PVAm in sulfite pulp (equal mixture of pine and beech) at pH 7.5 [31]. Wang and Tanaka reported that PVAm at 11% hydrolysis (reported as % amine groups) increased the wet/dry strength ratio of commercial hardwood bleached kraft pulp handsheets from approximately 5% to 30% [32]. Pelton and Hong investigated the properties of newsprint impregnated with PVAm and found that wet strength achieved almost 30% of the dry strength value [33]. Some key results from this work were that the wet strength was constant for up to 1 hr soaking and was not affected by the degree of hydrolysis between 56% and 100%. The wet tensile was higher when the paper was treated at pH 10 compared with pH 3 and pH 7.

Wet strength evaluation

The traditional laboratory approach to wet strength evaluation is to prepare hand sheets with resin-treated fibre suspensions and measure the wet tensile as a function of polymer content. Handsheets should be prepared to give a range of densities so wet tensile results can be compared at equal dry sheet density. This procedure requires independent measurement of resin retention and it is assumed that sheet formation is not influenced by wet strength resin addition.

In an attempt to learn more about the details of wet strength enhancement we have developed a model adhesion experiment in which two regenerated cellulose films are laminated together using the wet strength resin [34]. The ninety degree peel delamination force gives a measure of adhesion. If the laminate was never dried, the delamination, or peel force, corresponds to the wet-web strength; whereas, laminates which are dried and re-wetted simulate conventional wet strength measurements. Our approach is similar to that described by Ben-Zion and Nussinovitch who used wet cellulose as a model substrate for the characterization of skin adhesives [35]. The advantage of this approach is that the amount of polymer in the laminate can be carefully controlled, the measurements are rapid and reproducible, and the surfaces can be characterized before and after peeling. In this paper we show the influence of a number of parameters on the strength of cellulose-PVAm-cellulose laminates. From these results conclusions are made regarding the various contributions to wet adhesion.

RESULTS

Laminates were prepared by pressing and drying (50% RH, 23°C) a sandwich of two wet cellulose films with a layer of PVAm acting as an adhesive. A summary of the polymers used is given in Table 1. Two methods were used to apply the PVAm to the cellulose films. For most of the experiments the polymer solution was directly spread on the wet cellulose – we call this the **direct application** method. For some experiments, one or both cellulose films were exposed to a PVAm solution to give saturation adsorption – we call this the **adsorption application** method. Finally, for most experiments, the cellulose films were oxidized by NaClO with a NaBr and TEMPO (2,2,6,6-tetramethyl–1-piperidinyoxy radical) catalyst in order to introduce carboxyl and aldehyde surface groups. For testing, the dried laminates were soaked in aqueous solution and kept wet during the peel force measurements. Figure 1 shows the force versus displacement traces for three laminates which differ in the extent of oxidation. Adhesion increased significantly with cellulose oxidation.

A single peel force was extracted from each curve by averaging the data over the range of steady-state peeling which in most cases occurs between 10mm and 35mm. The three curves in Figure 1 illustrate that the noise within

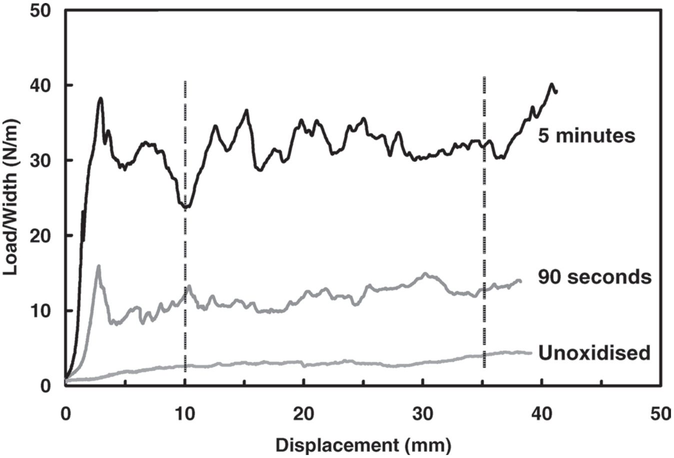


Figure 1 Force versus the displacement data for three wet laminates peeled at 90°. The labels indicate the residence time of the cellulose in the oxidizing solution and in the conditions are given in Figure 2. The dashed lines denote the range over which the data were averaged to give the peel force for the sample.

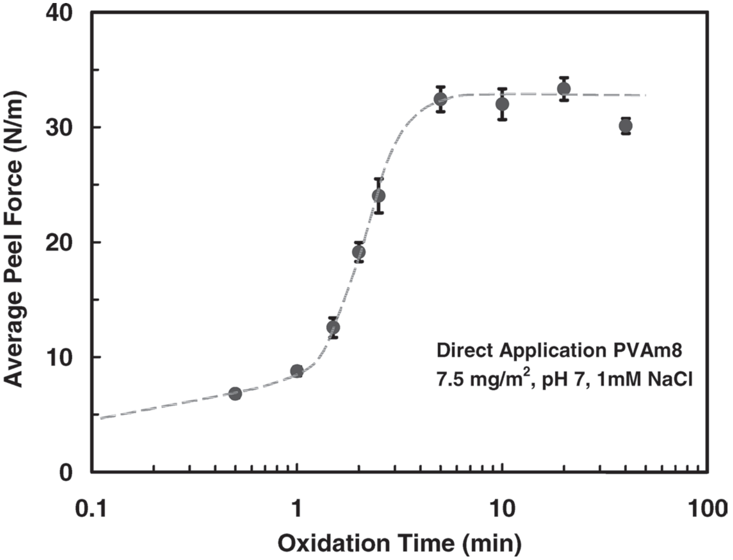


Figure 2 Peel force as a function of the time used to oxidize the cellulose membranes in TEMPO/NaBr/NaClO solution. See insert for details.

a peeling trace varies with sample properties. Most of the following results are based on 4 replicated experiments and the error bars were calculated as the standard error of the mean steady-state peel force.

The influence of surface oxidation is further illustrated in Figure 2 which shows the variation of peel force with the residence time of the cellulose in oxidizing solution. There appeared to be an induction period up to about 1 minute where peel force increased slowly. The largest increases in peel force occurred with oxidation times between 1 and 4 minutes. Longer oxidation times did not produce further changes in peel force. For most experiments, an oxidation time of 10 minutes was used, which is not in the sensitive regime of oxidation time.

Adhesion is usually sensitive to the quantity of adhesive in a joint. Figure 3 shows peel force as a function of PVAm which is expressed as mg/m^2 based on the macroscopic area of the adhesive joint (usually 20mm by 50mm). Peel force increased with PVAm coverage up to about 10mg/m^2 after which the peel force was approximately constant. Figure 3 also shows an individual point obtained using the adsorption application method. We did not know the corresponding coverage value; however, based on a PVAm adsorption study [36], we estimated that the equivalent of two adsorbed monolayers is

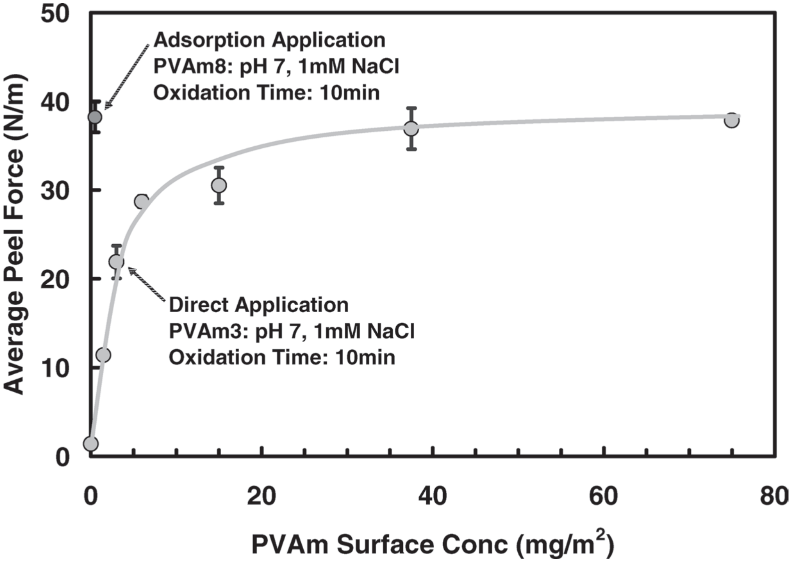


Figure 3 The influence of PVAm coverage on peel force. The cellulose was oxidized with TEMPO/NaBr/NaClO for 10 min.

about 0.5mg/m^2. Thus, for low surface coverage the adsorption application gives much stronger adhesion than the direct application.

Figure 4 shows the peel force as a function of PVAm molecular weight. The peel force was about 37N/m and was independent of molecular weight over the range investigated (34,000 to 1,500,000Da). The regenerated cellulose films, based on dialysis tubing, have fine pores. The molecular weight cut off (MWCO) is shown in the Figure 4 and the PVAm samples were too large to penetrate the membrane. The results have not yet been extended to low molecular weight PVAm, however, we anticipate that adhesion will decrease perhaps as shown in the dashed line since ethylenediamine, gives poor wet strength [37].

A basic assumption in this work is that a cellulose film laminated with PVAm is a model for fibre-fibre adhesion. One obvious difference between paper testing and our experiments is the length scale of the joint. Fibres are roughly 20 µm wide whereas the laminate strips are 20mm wide. It could be argued that during the soaking step, water transport into the laminate and PVAm diffusion out of the joint will be artificially slow in the laminates. A series of experiments were conducted in which the only variable was the

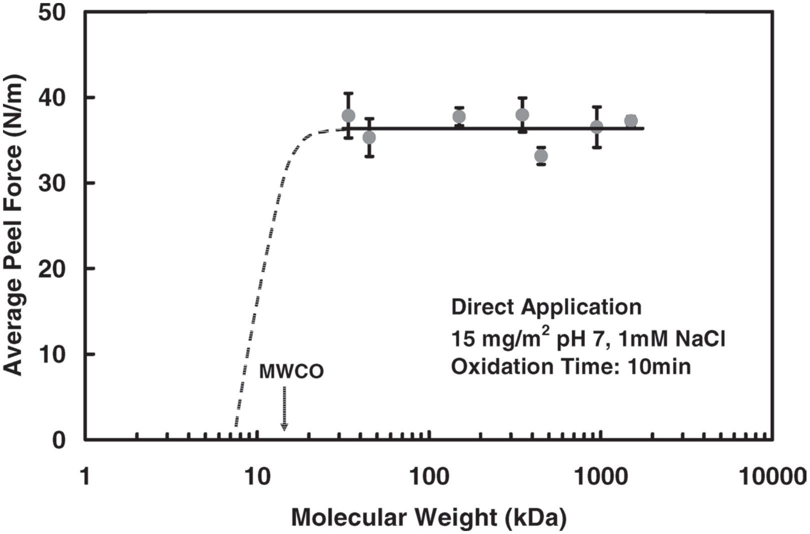


Figure 4 The effect of PVAm molecular weight on the laminate strength of regenerated cellulose membranes.

laminate soaking time before peeling and the results are summarized in Figure 5. Our standard soaking time is 30min. The shortest soaking time in this series of experiments was 10min and the longest was 65 days. There was a slight decrease in peel force between the first and second point followed by an increase in peel adhesion with soaking time. Thus there were no slow processes which lower adhesion such as diffusion of polymer out of the joints.

PVAm is prepared from the hydrolysis of PNVF (see Scheme 1). In previous work we measured the wet strength of commercial newsprint impregnated with PVAm of varying degrees of the hydrolysis [33]. PNVF (i.e. approximately 0 degree of hydrolysis) gave no wet strength improvement whereas newsprint wet tensile increased to a maximum value with 56% hydrolysis; higher degrees of hydrolysis gave little further advantage at polymer retention values greater than 2%. The results from the corresponding cellulose delamination experiments are shown in Figure 6, which includes data obtained using both application methods (direct and adsorption) for treating the cellulose films with PVAm. In agreement with our previous handsheet work, there was little advantage having degrees of hydrolysis greater than 55%. Furthermore, the two application methods gave the same results.

In an effort to gain some insight into the factors controlling adhesion,

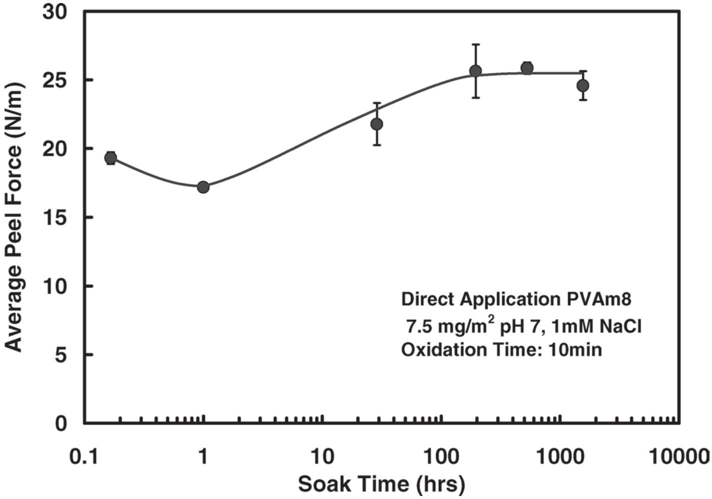


Figure 5 Change in the peel force with soaking time of the laminates in 1mM NaCl prior to peeling.

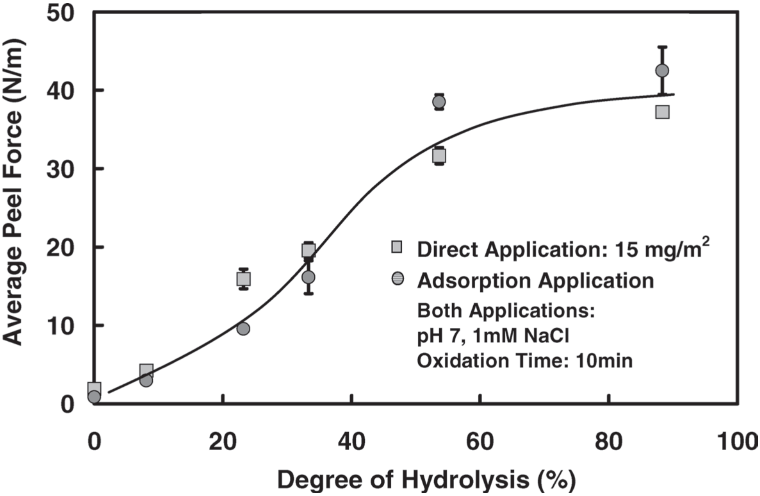


Figure 6 The effect of PVAm hydrolysis degree on the delamination force. The molecular weight of the parent PNVF was 1,500 kDa.

measurements were made as a function of pH and drying temperature. Figure 7 shows adhesion as a function of drying temperature. The higher temperature data were nosier and the adhesion increased slightly with drying temperature. Gravimetric analysis indicated that the laminates were about 20% water after conditioning at 50% RH, 23°C, which corresponds to the lowest point in Figure 7. Although this seems like rather ineffective drying it is significant, as laminates which were not conditioned gave no measurable wet strength. Thus, the drying stage is critical to the wet-strength mechanism and as such PVAm is unlikely to increase wet web strength.

Figure 8 shows the influence of pH on wet adhesion for both PVAm application methods. It should be noted that there were slight differences in the PVAm used in the two sets of experiments – see the figure captions for details. The peel force was a strong function of pH. The direct application data showed a sharp drop below a pH of 2.75 and a gradual decline from pH 5 to 12. The adsorption application results showed the same trends although the maximum adhesion values were higher. Any explanation of the mechanisms of PVAm wet-strengthening must account for the results in Figure 8. The adhesion was approximately constant from pH 3 to 9, whereas at pH 3 nearly every amine group on PVAm is charged (protonated), while at pH 9 the

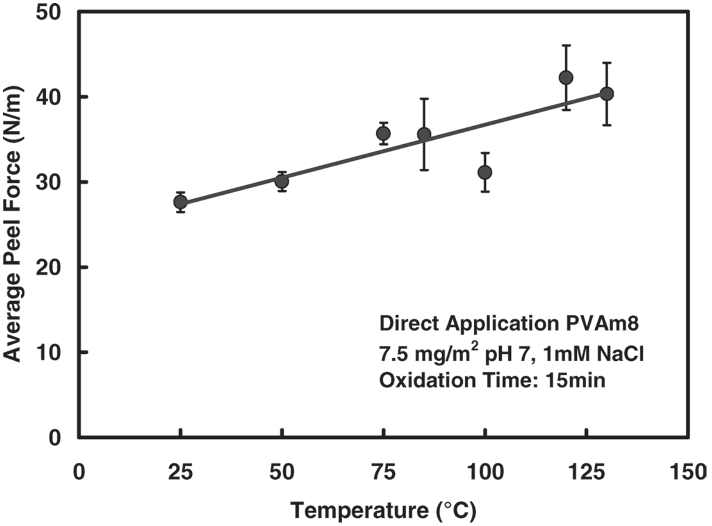


Figure 7 The influence of laminate drying temperature on adhesion. The cellulose was oxidized for 10min and the laminates were heated for 20 min.

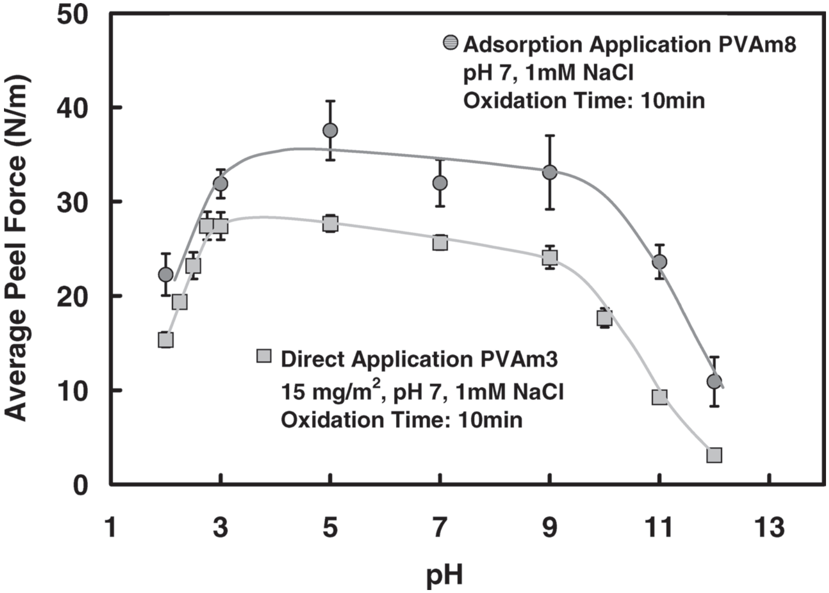


Figure 8 The influence of pH on PVAm adhesion. The same solution pH was used for polymer application and pre-test soaking. The squares represent direct application of PVAm3 at a coverage of 15 mg/m^2. The circles represent the adsorption application of PVAm8 on only the top film.

PVAm is nearly uncharged. Thus, the wet adhesion was independent of the extent of PVAm protonation (i.e. the charge content) over a broad range.

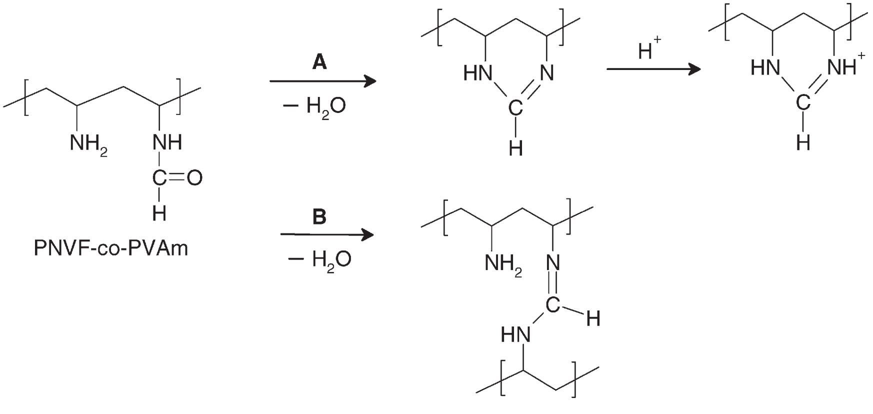
DISCUSSION

Conventional wet strength resins such as PAE and glyoxylated polyacrylamide function by forming covalent grafts between the resin polymer chains and the cellulose fibre, and by crosslinking themselves giving a covalently bonded polymer network in the fibre joint. At first glance, PVAm does not appear capable of crosslinking or grafting to cellulose. Hence, why does it give wet strength? It is convenient to separately consider covalent bonds and physical bonds.

PVAm Covalent bonding chemistries

The results in Figure 3 show that good adhesion was achieved with a PVAm coverage of 70mg/m^2. This corresponds to approximately 50 layers of PVAm chains, which in turn, means the cohesive strength of the PVAm layer must be high. This is difficult to understand because a cast PVAm film will dissolve in water suggesting that PVAm does not spontaneously crosslink. There is one potential type of bond between PVAm chains. The formamide groups on partially hydrolyzed PVAm can covalently bond to neighbourging amine groups (see Scheme 3) to give a ringed amidine structure (route A). Alternately, the formamide group can react with a non-neighbourghing amine on the same chain or another chain (route B) to give an amidine linkage. The amidine is thermodynamically stable due to the delocalization of the double bond and, therefore, route A is preferred over route B. Reaction route A has been found to occur during the palladium catalyzed hydrolysis of PNVF in water at high temperatures [38]. Reaction route B is facilitated at lower temperatures when PVAm reacts with acetaldehyde (a hydrolysis product) or an additional aldehyde cross-linker [39]. It seems unlikely that amidine groups formed during the laminate preparation and less likely that cross-linking occurred via route B. Therefore, we conclude that PVAm crosslinking does not occur, with the possible exception of during the high drying temperature experiments (Figure 7).

While there is little possibility for covalent cross-links, PVAm will graft onto cellulose films. The only potentially reactive groups on pure cellulose are

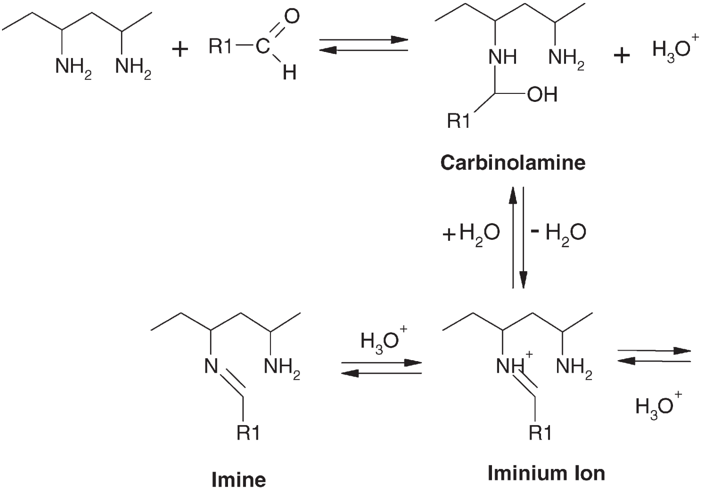


Scheme 3 The reaction of an amide with an amine to give an amidine. Route A gives a ringed amidine. Only route B gives a crosslink between chains.

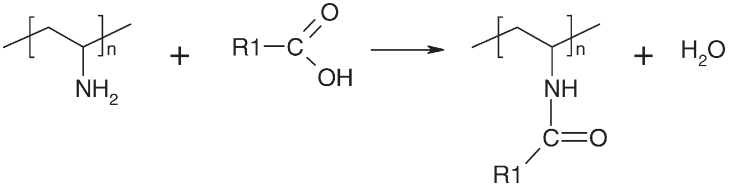
the many hydroxyl groups and the hemiacetal/aldehyde group at one end of each cellulose chain. These few terminal aldehyde groups, which are accessible to PVAm, will react with amines in PVAm, therefore, we conclude that PVAm should not form many covalent bonds to untreated cellulose.

PVAm gave low adhesion to untreated cellulose whereas TEMPO oxidized cellulose gave strong adhesion. This treatment converts the C6 cellulose hydroxyl to carboxyl and aldehyde groups which will react with the amine groups on PVAm. Amines will couple to aldehydes to form imines – see Scheme 4. This is a reversible reaction that occurs at room temperature in water through the carbinolamine intermediate and is catalyzed by acid. Typically, an excess of acid will reduce the rate of imine formation due to the protonation of the amine and reduction in the initial nucleophilic attack. Therefore, in general, the rate curve will display a bell shape with an optimal pH range of 4–5 [40, 41]. Imine formation has been proposed as an important contribution to the ability of chitosan to increase wet strength [7].

Imines can react with amine groups to give aminals [42, 43]. If the imine shown in Scheme 4 reacts with a neighbouring amine group then the result is the six-membered aminal. This product is thermodynamically preferred due to the structure, however both imines and aminals are susceptible to hydrolysis at moderate temperatures.



Scheme 4 Reaction of an amine with an aldehyde to form an aminal through two possible routes.



Scheme 5 Condensation of an amine with a carboxyl to give an amide. This reaction would proceed slowly between cellulose bound carboxyl groups and amino groups on PVAm and thus contribute little in wet strength development.

TEMPO oxidation also gives carboxyl groups on the C6 carbon of cellulose. In an initial investigation we showed that the carboxyl content was 2meq/100g cellulose after 30min of oxidation [34]. Amines will condense with carboxylic groups to give amide groups – see Scheme 5. Amide formation generally requires temperatures greater than 150 °C to produce a significant yield of amide and usually occurs under conditions in which free water is removed [44]. Amide formation at moderate temperatures (70–100°C) does occur [45]. Furthermore, amines couple to formic acid under mild conditions. Nevertheless, it seems unlikely that amide formation is significant in our experiments because the contact times are short and the conditions mild.

In summary, we propose that no crosslinks form between PVAm chains, whereas imine and aminal bond formation do contribute to PVAm-cellulose wet adhesion. However, the occurrence of strong adhesion from pH 3 to 9 (Figure 8), which is beyond the range of imine or aminal formation, suggests that physical bonding is also significant.

PVAm Physical bonding

The chemical properties of PVAm are a strong function of solution pH. At pH 3 virtually every primary amino group is protonated ($-NH_3^+$) giving the polymer a high positive charge whereas at pH 10.5 most of the amine groups are not protonated ($-NH_2$). Between these two extremes the degree of protonation decreases linearly with pH – this is illustrated in Figure 9 [46]. Therefore, at low pH we would expect PVAm to interact with cellulose, or other surfaces, by electrostatic attraction to negatively charged surface sites.

The oxidized cellulose films will have a negative surface charge due to carboxyl groups. We would expect a fraction of the charged carboxyls to give the pH dependence shown in Figure 9. This figure also shows the pH dependence of PVAm ionization. The overlap area indicates the pH range over which electrostatic interactions should occur.

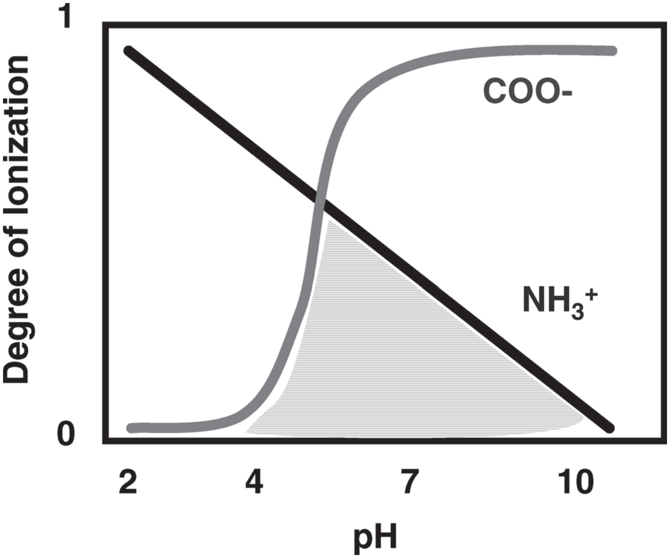


Figure 9 Schematic illustration of pH dependence of the fraction of charged amine groups on PVAm and of charged carboxyl groups on oxidized cellulose.

In summary, we propose that PVAm strengthening is due to a combination of covalent bond formation and electrostatic bonding. We hypothesize that covalent bonding is the most important. Based on the current data, it is impossible to decouple the effects of electrostatic and covalent bond formation. Resolving this unanswered question is important since it will point to the best strategies for fibre surface modification to optimize PVAm wet strengthening performance.

CONCLUSIONS

The main conclusions from this work are:

1. PVAm gives adhesion between wet cellulose films provided that the laminates were conditioned at 23°C and 50% RH. This is in agreement with published handsheet data. The adhesion results do not predict an improvement in wet web strength.
2. Although drying is important, adhesion is weakly dependent on drying temperature over the range 23 to 130°C (Figure 7).

3. The primary amine groups on PVAm are the active agents for wet strength since adhesion increases with PVAm amine content.
4. The oxidation of cellulose gave a six-fold increase in wet adhesion supporting the hypothesis that imine and aminal bonds between cellulose and PVAm contribute to wet strength.
5. Above monolayer coverage, adhesion is virtually independent of PVAm content (Figure 3) and molecular weight (Figure 4) suggesting that wet PVAm has high cohesive strength even in the absence of covalent bonds between neighbouring PVAm chains.
6. Because peel strengths are independent of soaking time up to months, the cellulose laminates were tested under conditions of equilibrium swelling. Furthermore, the slow diffusion of PVAm from the joints was not significant.
7. Wet adhesion was remarkably independent of pH between 3 and 9 suggesting that in addition to covalent bonding, electrostatic interactions between carboxyls and amines contributed to wet adhesion.

EXPERIMENTAL

Polymers

Polyvinylamine, PVAm, was supplied by BASF (Aktiengeselschaft, Germany). PVAm of varying molecular weights were prepared by the base hydrolysis of poly(N-vinylformamide) – see Scheme 1. So, in addition to molecular weight, an important variable is the degree of hydrolysis (usually expressed as a mole percent). All polymers were supplied at a 95% degree of hydrolysis as measured by formic acid formation. All polymers were purified by exhaustive dialysis against distilled water. The resulting dilute solutions were dried in a Heto Drywinner vacuum freeze drier and stored in a desiccator at room temperature. The specific charge content of the polymer was determined by conductometric titration with 0.1N NaOH using a Burivar-I2 Automatic Buret (minimum injection volume 1μL, ManTech Associates) controlled by PC-Titrate software (version 2.0.0.79). Proton NMR was used to determine the degree of hydrolysis. The properties of the polymers used in this investigation are summarized in Table 1.

PVAm8 (see Table 1) was prepared by further hydrolyzing PVAm3. In this procedure 15g of PVAm3 was added to a round bottom flask and diluted with deionized water to 3wt%. Concentrated NaOH was added to give a final concentration of 5wt% (1.25 N). The reaction vessel was then placed in an oil bath on a magnetic stirrer (IKA RET Basic) with temperature control (IKA ETS D4 fuzzy) and set at 78°C. Air was purged from the system using a low

Table 1 List of polymers used in this study and some properties.

Designation	Mw (kDa)	% DH	Charge Content (meq/g)
PVAm1	34	86.3	13.60
PVAm2	70	81.4	13.40
PVAm3	150	96.6	12.40 ± 0.57
PVAm4	300	96.1	–
PVAm5	350	–	14.00
PVAm6	950	90.5	13.20
PVAm7	1500	94.6	13.68
PVAm8	150	>98	13.2 ± 0.76
PVAm9	1500	1.0	–
PVAm10	1500	8.1	–
PVAm11	1500	23.2	–
PVAm12	1500	33.3	–
PVAm13	1500	53.6	–

flow of nitrogen gas. The reaction continued for 4 days under constant stirring and positive nitrogen pressure. Finally the solution was purified by dialysis. No further formamide groups could be detected by proton NMR.

Cellulose preparation and modification

Regenerated cellulose dialysis tubing (Spectra/Por® 4 product No:132682 12kDa MWCO, Spectrum Laboratories, Inc.) was cut to the following dimensions: top membrane (2cm by 6cm) and the bottom membrane (3cm by 6cm). Samples were cut with the long axis in the roll direction, and only the interior surface of the tubing was used to study adhesion. Cellulose film strips were soaked in room temperature water for 24hrs to remove any preservatives (glycerine). The cellulose films were then rinsed thoroughly and stored in water with a small amount of methanol (to prevent spoilage) at 4°C.

Most of the cellulose films were oxidized with 2,2,6,6-tetramethyl–1-piperidinyoxy radical (TEMPO), NaBr and NaClO (11–14%) [47] all supplied by Sigma-Aldrich following Kitaoka's method [19]. The concentration of TEMPO/NaBr was fixed at 0.034g/L and 0.34g/L respectively and the concentration of sodium hypochlorite was 3wt% based on dry cellulose. All reactions took place at 23°C under mild stirring (magnetic stirring bar) in a 1L glass beaker treating up to 7g cellulose. The pH was maintained at 10.5 by sodium hydroxide and the oxidation was stopped by adding ethanol to the suspension. The cellulose was removed and rinsed first in ethanol and then repeatedly with deionized water. The treated films were stored at 4°C with a small quantity of methanol.

Polymer application

Two methods were used to apply PVAm to the cellulose films – **direct application** and **adsorption application**. For the adsorption application method, the top cellulose film was covered in 0.6mL of a solution of 0.5mg/mL PVAm dissolved in 1mM NaCl with the pH adjusted to the desired value. After soaking for 30 min the films were rinsed gently for 5min in pH adjusted 1mM NaCl solution. We assume that by rinsing off excess polymer that the resulting cellulose films were coated with a saturated monolayer of adsorbed PVAm [22, 48]. The laminates were constructed by first placing the wet bottom membrane on a blotting paper. A 40 × 12.7mm long piece of Teflon tape (G.F. Thompson Co. Ltd, TWB480P) was placed across one end of the bottom membrane (see Figure 10, right hand side). The purpose of the Teflon tape, which was removed before peel testing, was to give two cellulose film tails for attachment to Instron clamps and to give a uniform crack in the laminate. In the next step the top membrane was placed on the bottom membrane, followed by blotting paper. The wet laminate was pressed between blotting paper at 89kN and room temperature for 30min. After pressing, the laminates and blotting paper were equilibrated at constant temperature (23°C) and humidity (50%) for at least 12 hours under no load.

In the direct application method, the bottom cellulose membrane was placed on a stainless steel plate and excess surface water removed by dabbing with a lint free tissue. The Teflon tape strip was placed at the edge of the

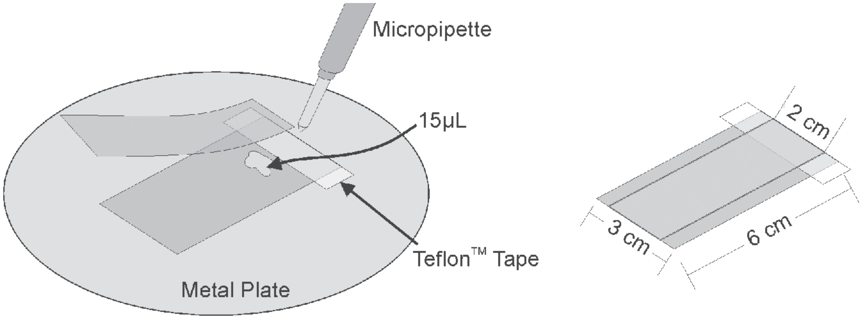


Figure 10 Illustration showing the direct application of PVAm (left) and the final dimensions of the laminates used in this study (right).

bottom membrane and a 15µL drop of aqueous PVAm was applied using a 20µL micropipette (Gilson) onto the base membrane near the Teflon tape (see Figure 10, left-hand side). The top membrane was progressively placed over the bottom membrane starting at the end with the Teflon tape. If done carefully, the 15µL polymer solution droplet uniformly spread between the top and bottom membrane with negligible loss of polymer solution. The PVAm solutions varied in concentration, salt content (NaCl) and pH. Base conditions were 0.1wt% PVAm, 1mM NaCl, and pH 7. The laminated membranes were then dried and conditioned in the same fashion as described previously.

Wet adhesion testing

Before testing, the laminated membranes were soaked for 30min in 50 mL of deionized water at the ionic strength and pH of the applied polymer solutions, after which excess water was removed by uniform pressing (2.4kg roll wheel) between two pieces of blotting paper. The wet, laminated membranes were then mounted using a 4cm wide fluid resistant two sided tape (3M Polyethylene Medical Double Coated Tape; Model No: 1522) onto a 14cm diameter, 40mm wide aluminium peeling wheel running on SKF-6,8–2RS1 radial bearings – this configuration gives a 90 degree peel angle [49]. The wheel was fixed to the bottom jaw of an Instron 4411 universal testing system (Instron Corporation, Canton, MA) fitted with a 5N ±0.005N load cell. The top membrane was separated from the base membrane at the edge with the Teflon tape and clamped into the upper jaw of the Instron. The samples were tested at a crosshead rate of 20mm/min. The steady-state force was taken for each membrane with the result divided by the membrane width (20mm) to give a width-normalized force in units of N/m.

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Transcription of Discussion

THE MECHANISM OF POLYVINYLAMINE WET-STRENGTHENING

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Tom Lindström STFI-Packforsk AB

If I understood it correctly, your chemical reaction takes place at room temperature. Does it also take place in the wet state, or only in the dry state?

John-Louis DiFlavio

The reaction between the amine and carbonyl, is that what you mean? We believe the reaction takes place as the laminate is drying. They will react in water, and the reaction is reversible of course, so there is an equilibrium between the products and reactants, but personally I believe, when it is drying, you have more intimate contact between these amines and aldehydes on the surface. That is what will drive the formation of covalent bonds; which would not be accessible for hydrolysis when you add water, since they are more tightly packed.

Tom Lindström

So what happens if you apply heat?

John-Louis DiFlavio

Our results show (we have only done it at pH 7) that if it is heated we get slightly better adhesion, but it is not a 10-fold increase, it's about a 3-fold increase. So if we cure it, if we add more heat, we get higher adhesion, but it is not a colossal increase.

Tom Lindström

I think we should be concerned about toxicity of this stuff if it reacts at room temperature.

Alan Button Buttonwood Consulting

One concern I have about this general testing method is something I think we need to pay attention to. As you modify the cellulose, as you have in some of your experiments, I would guess that you are also modifying mechanical properties of your cellulose film. If you look at the mechanics of this, the actual modulus of the film becomes an important part of the testing outcome; apart from what you do with the interface. So one thing I would recommend is that you look at what kind of modulus changes you have in the film. You can look at a simple tensile test to bring in that information and refine the testing technique and interpretation of the outcome. Another question is what is the nature of the failure? What is the range of failures you see?

John-Louis DiFlavio

So, by "nature of failure" you mean whether we are looking at adhesive/cohesive failure? We have imaged this system using fluorescently modified polymer. We have looked at the interface and we find that this seems to be (especially when you add a thick layer of polymer) a mixed mode of failure between polymer and the cellulose and through the polymer. The actual surface of the cellulose is not smooth, rather we have a wavy surface and we suspect that, if we have a deep valley, then there might be failure mode differences in that region.

Alan Button

One of the things that happen with cellophane film is that gas bubbles are trapped below the cuticle on the surface. When you get failure sometimes you're just pulling out this unsupported area. Even though there are a lot of complications, I love this substrate for working the way you are.

John-Louis DiFlavio

I would like to make a comment in regards to the mechanical testing. We did measure this as a function of the oxidation time and actually the modulus decreased as we did tensile tests. We found that as we increased the oxidation time eventually we started to see a very sharp drop in the mechanical properties; but within the initial range of our adhesion increase, we did not see a very drastic change. As we oxidized further, producing more carboxyl groups and maybe a higher degree of swelling, we measured the mechanical properties and we saw a big difference.

Glyn Jones Arjo Wiggins Ltd

I have been studying ink adhesion based on inks with carboxyl functional groups on polyethyleneimine, but solely outside of an aqueous phase. Initial results seem to suggest that it is an electrostatic interaction. Do you know how much of a contribution the aqueous phase has to dictate covalent interactions?

John-Louis DiFlavio

I think the presence of water will inhibit covalent bond formation; in fact many products between carboxyl and amine or aldehyde and amine are generally catalyzed if you remove the water, as these are condensation reactions. So, if you have water there you are going to prevent formation of these covalent bonds, but if you dry the system, if you start removing water, then you get a denser environment and I believe you will push equilibrium to the product side. So, I think the water will reduce the amount of covalent bonds you have.

Glyn Jones

So, have you actually assessed this without having to pre-wet before doing the peel test to prove that point?

John-Louis DiFlavio

You mean peeling these membranes without wetting them? The actual problem with that is the cellulose of this membrane is very brittle when it is dry. So, we actually cannot peel it, we cannot fix it to the wheel at all as it will separate easily, so it is too stiff in that regard. So right now our testing is exclusively in the wet state and that is all we have looked at right now.

Discussion

John Roberts

Have you been able to quantify the relative amounts of aldehyde and carboxylic acid groups resulting from the TEMPO oxidation treatment?

John-Louis DiFlavio

That is a part of our continued work. I think that, once we can put some numbers to the amount of surface groups on the cellulose, then we can really confirm which mechanisms are more important.

John Roberts

So, the reaction is a surface reaction, it is not a bulk reaction presumably?

John-Louis DiFlavio

Again, this is a membrane. So you are looking at what is happening within, as well as on the surface, but we believe that reactions *near* the surface should be the only reactions that are important to the adhesion.

Christian Schmid Hewlett-Packard

Have you ever seen the polyvinylamines turn yellow in any stage of your experiments?

John-Louis DiFlavio

Yes, actually what we do when we get raw samples from BASF is we hydrolyze and purify them, then we freeze dry them and sometimes they turn out as yellow crystals and sometimes they turn out as white crystals or white powder. First, we suspected that maybe somebody put something else on the freeze drier and contaminated our samples, but it could also be a condition of whether the polymer is in the hydrochloride state or whether it is in the de-protonated state.

Christian Schmid

We see that a lot with primary amines, PEI is one of the worst, they turn yellow when on the paper, so I was just wondering if you saw that.